

## Commentary

# Femtochemistry uncovers the nature of electron transfer reactions

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Electron transfer reactions are among the most ubiquitous and elementary of all chemical processes, with wide-ranging implications throughout many areas of chemistry, physics, and biology [refs. 1, 2 (and references therein), 3, and 4]. In its simplest form, no bonds are broken, and an electron is shuttled between two ionic species in what is termed a self-exchange or cross-reaction. Modern understanding of the rates of such processes is derived from the theoretical work by Marcus (5, 6), who showed how a dielectric continuum approximation for the solvent, in combination with the Franck-Condon principle and considerations of the free energy of reaction, could be used to quantitatively account for the wide-ranging rates observed for such transformations. Thereafter, the continuum model was replaced with a molecular approach in which the solvent was first treated as a collection of dipoles, whereas later, both the solvent molecules and reactants were expressed in terms of a general charge distribution. Carefully designed experiments by many groups verified the numerous predictions of the theory and have led to intense interest in the molecular aspects of the processes. The field remains very active, with current attention being given to such problems as unraveling the rates and mechanisms of long-distance intramolecular charge transfer through utilizing the concepts of inserting molecular spacers between the donor and acceptor ends of a molecule (see for example, refs. 7 and 8).

Beyond searching for an understanding of the molecular details involved in acid–base and related charge-transfer reactions is the large field of biochemistry, for which numerous charge-transfer questions arise, including those related to charge migration in DNA (9–11), processes in photosynthetic reaction centers (12), and other protein systems (13, 14). Photoinduced electron transfer plays a major role in triggering numerous chemical and biological processes, and there is growing interest in elucidating the molecular details of the initial steps, particularly in cases in which there is concomitant bond disruption/rearrangement taking place. In terms of photophysical processes, a particularly relevant phenomenon bearing on reactive charge transfer comes from early considerations by Mulliken (15) and Benesi and Hildebrand (16), who observed new absorption bands in solutions of iodine and various organic media, giving rise to what were described as charge transfer complexes. Identifying the fundamental steps involved in the charge transfer and subsequent dissociation has led to a major beginning in a molecular understanding of these important phenomena in which electron and atom transfer, mediated by caging dynamics, take place (17). In these and related processes in which multiple reaction steps are possible, major questions arise about their concerted/synchronous versus step-wise mechanisms. In pioneering studies of purely molecular dissociation processes, Zewail and coworkers have already shed considerable new light on these important phenomena (1), leading to an in-depth understanding of many fundamental reactions such as Norrish type I photoinduced reactions (18–20), for example, in which questions of the simultaneity of photophysical events come into play.

Because the processes of thermal electron transfer in natural environments are very complex, researchers are seeking ways to study the fundamental aspects of these phenomena in simplified model systems by using well characterized optical pulses to interrogate the reaction. The unique ability to probe electron transfer and concomitant bond making and breaking through ultrafast studies of processes initiated by femtosecond photoexcitation and followed through femtosecond probe experiments has been demonstrated by Zewail and coworkers (21). An extension to their earlier work on the benzene iodine system is reported on pages 2602–2607 of issue 6 of the *Proceedings* by Zhong and Zewail (22), in an article entitled “Femtosecond dynamics of dative bonding: Concepts of reversible and dissociative electron transfer reactions.” The new study provides a prototypical case of elementary processes involving rapid electron redistribution, with concomitant bond making and breaking being jointly operative. The authors have shown that the dynamics of electron transfer occur by two elementary pathways and that the electron transfer is reversible. They also provide, from the vectorial dynamics of the reaction, the geometry of the transition state.

In considering this article, two questions may come to the readers' mind. First, why femtoseconds? Second, why gas-phase experiments? It has been said, and properly so, that all chemistry involves femtochemistry. Indeed, as we know, the vibrational motion of nuclei is the fundamental motion that characterizes chemical bonds and ultimately determines the reaction dynamics at the molecular level. Time scales for vibrations are typically subpicosecond. Only with the time resolution and coherence provided by femtosecond laser pulses can we observe chemical reactions in real time as they proceed along the reaction path from reactants, via the transition state (23), toward products. Questions related to gas-phase investigations and their applicability to understanding the condensed state naturally arise. First, it should be recognized that studies in the gas phase provide unprecedented detail of the mechanisms involved in the photoexcitation and ensuing reaction processes. A direct examination of the transfer processes is enabled. Second, through examining molecular complexes, the process of caging also can be investigated. Although time scales between the gas and the condensed state may differ, it is worth recognizing that, even in the condensed state, because of fluctuations and excursions of surrounding solvent media, only a very few solvent molecules are located in close proximity to the initial center of excitation during the photoexcitation and electron reorganization event. Only through interrogating isolated systems can one hope to identify the full evolution of the intermediate states involved and the ultimate outcome of processes that occur in the condensed state, though these, of course, become mediated at long-times through diffusion and further energy transfer to the surrounding solvent media.

In describing the energetics and dynamics of a chemical bond, Lewis *et al.* (24), Pauling (25), and Mulliken (26), among others, developed the concept of considering both its coexist-

ing covalent and ionic character. In some chemical systems, the ionic and covalent potential energy surfaces of a specific nuclear coordinate lie close in energy and may curve cross, which will influence the dynamics of the reactions of interest. A simple example of this is the case of NaI in which the ground state ionic curve crosses with the covalent curve of the first excited state. Both the ground state and the excited state possess the same symmetry, which forces an avoided crossing on the potential energy surface. The resulting electronic structure along the reaction coordinate of the upper quasibound potential well formed from curve-crossing changes from being covalent at short nuclear distance to being ionic at larger distances. As shown by the Zewail group (27), when the ground state NaI molecule is excited with a femtosecond laser pulse to the first excited state, the wavepacket, initially prepared on the repulsive covalent potential, propagates within the quasibound well. As it propagates, the bonding of NaI oscillates from covalent to ionic character. This coherent wavepacket motion is directly monitored by a second femtosecond laser. In the present study (22), this method has been applied to the more complicated diethyl sulfide iodine system and was used to unravel the mechanism of the dissociative electron transfer reaction. (see Fig. 1)

As described in the paper by Zhong and Zewail (22), the application of molecular-beam techniques enables the formation of a van der Waals complex in a well described geometry, in this case,  $(C_2H_5)_2S \cdot I_2$ . A femtosecond pump pulse is used to excite the complex at a well defined initial time to a charge transfer state [ion pair formation:  $(C_2H_5)_2S$  donates an electron to  $I_2$ ], and the evolution from ionic to covalent potential and the reversible dissociative electron transfer are monitored by detecting the photofragment, I atom, in a kinetic energy time-of-flight mass spectrometer. Both the angular and velocity distribution of the photofragment are resolved by recording the ion signals at different polarization of the photolysis laser, enabling two different photodissociation channels to be identified: dissociative electron transfer and dissociation from the intermediate  $(C_2H_5)_2S \cdot I$  complex.

Elucidating the details of processes involving electron transfer in general, and concomitant electron transfer and chemical reaction in particular, has major impact on understanding phenomena of great interest to numerous fields. In a very recent work (28), for example, the unidirectional photoinduced electron transfer seen in bacterial photosynthetic reaction center has been emulated by a synthesized model system. Weak fluorescence was observed because of a rapid photoinduced electron transfer from an amine group to a fluorophore. When the amine group is

protonated, electron transfer is arrested, and the fluorescence recovers. The general conclusion is that the excited state dipole of the fluorophore directs the electron traffic, being influenced by the associated protonation step.

In addition to the field of biology, there is the potential for considerable impact on the field of photosynthesis. One of the long-term goals of studying the elementary electron transfer processes is to develop an understanding of the photoinduced electron transfer reaction to a stage that will ultimately enable the design of model systems for capturing and storing solar energies by converting the solar energy into chemical potentials.

In summary, femtosecond-resolved measurements on the dynamics of electron transfer and bond breaking are being used to uncover nonequilibrium relaxation effects, an area that presents special challenges to an understanding of the behavior of coupled processes. Gas-phase experiments on isolated complexes are particularly valuable in unraveling the detailed mechanisms involved. Additionally, investigations of electron transfer and concomitant chemical reactions in polymers, synthetic materials, and biomolecules also offer the prospect of gaining substantial new insights into the nature of the electron transfer process. We can expect even further major advances in a fundamental understanding at the molecular level of these important processes to be derived from the field of femtochemistry.

1. Sundström, V., ed. (1996) *Femtochemistry and Femtobiology* (Imperial College Press, London).
2. Fox, M. A., ed. (1992) *Chem. Rev.* **92**, 365–368.
3. Kelly, S. O. & Barton, J. K. (1999) *Science* **283**, 375–381.
4. Jortner, J. & Bixon, M. (1998) *Collect. Czech. Chem. Commun.* **63**, 1285–1294.
5. Marcus, R. A. (1993) *Engewandte Chemie* **32**, 1111–1222.
6. Marcus, R. A. (1956) *J. Chem. Phys.* **24**, 966–978.
7. Nocera, D. C., Winkler, J. R., Yokum, K. M., Bordignon, E. & Gray, H. B. (1984) *J. Am. Chem. Soc.* **106**, 5145–5150.
8. Jortner, J. & Bixon, M., eds. (1999) *Advances in Chemistry and Physics* (Wiley, New York).
9. Jortner, J., Bixon, M., Langenbacher, T. & Michel-Beyerle, M., E. (1998) *Proc. Natl. Acad. Sci. USA* **95**, 12759–12765.
10. Fiebig, T., Wan, C., Kelly, S. O., Barton, J. K. & Zewail, A. H. (1999) *Proc. Natl. Acad. Sci. USA* **96**, 1187–1192.
11. Lewis, F. D., Wu, T., Zhang, Y., Letsinger, R. L., Greenfield, S. R. & Wasielewski, M. R. (1997) *Science* **277**, 673–676.
12. Stowell, M. H. B., McPhillips, T. M., Rees, D. C., Soltis, S. M., Abresch, E. & Feher, G. (1997) *Science* **276**, 812–816.
13. Telford, J. R., Wittung-Stafshede, P. & Winkler, J. R. (1998) *Acc. Chem. Res.* **31**, 755–763.
14. Nocek, J. M., Zhou, J. S., Forest, S. D., Priyadarshy, S., Beratan, D. N., Onuchic, J. N. & Hoffman, B. M. (1996) *Chem. Rev.* **96**, 2459–2489.
15. Mulliken, R. S. (1952) *J. Am. Chem. Soc.* **74**, 811–824.
16. Benesi, H. A. & Hildebrand, J. H. (1949) *J. Am. Chem. Soc.* **71**, 2703–2707.
17. Gaspardt, P. & Burghardt, I., eds. (1997) *Chemical Reactions and their Control on the Femtosecond Time Scale* (Wiley, New York).
18. Kim, S. Y., Pederson, S. & Zewail, A. H. (1995) *J. Chem. Phys.* **103**, 477–480.
19. Buzza, S. A., Snyder, E. M. & Castleman, A. W., Jr. (1996) *J. Chem. Phys.* **104**, 5040–5047.
20. Zhong, Q., Poth, L. & Castleman, A. W., Jr. (1999) *J. Chem. Phys.* **110**, 192–196.
21. Cheng, P. Y., Zhong, D. & Zewail, A. H. (1996) *J. Chem. Phys.* **105**, 6216–6248.
22. Zhong, Q. & Zewail, A. H. (1999) *Proc. Natl. Acad. Sci. USA* **96**, 2602–2607.
23. Zewail, A. H. (1988) *Science* **242**, 1645–1653.
24. Lewis, G. N. (1966) *Valence and the Structure of Atoms and Molecules* (Dover, New York).
25. Pauling, L. (1967) *The Nature of the Chemical Bond* (Cornell Univ. Press, New York).
26. Mulliken, R. S. & Person, W. B. (1969) *Molecular Complexes: A Lecture and Reprint Volume* (Wiley Interscience, New York).
27. Rose, T. S., Rosker, M. J. & Zewail, A. H. (1988) *J. Chem. Phys.* **88**, 6672–6673.
28. de Silva, A. P. & Rice, T. E. (1999) *Chem. Commun.* **2**, 163–164.

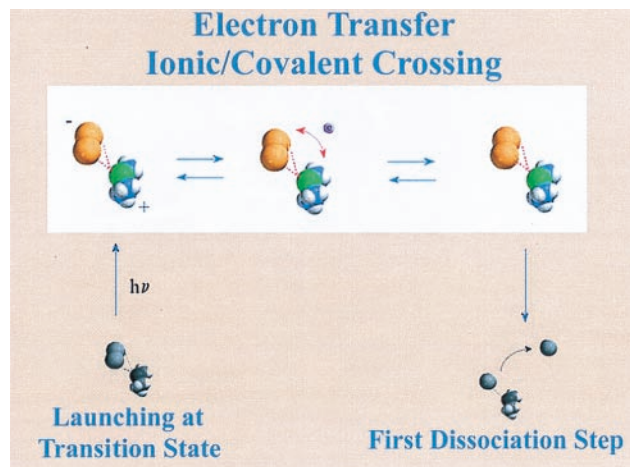


FIG. 1. Electron transfer in the diethylsulfide/iodine system at the ionic/covalent curve crossing.